Thermo- and photo-reversible reactions for the preparation of smart materials : smart rubbers and recyclable shape memory polymers

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1. Introduction

Crosslinking of polymeric matrices allows to impart to the resulting materials improved properties such as larger wear resistance, increased stiffness or decreased creep. It also gives rise to new materials such as hydro- or lipogels or shape memory materials. Classical chemical crosslinking relies on the formation of multiple strong and irreversible chemical bonds between the polymer chains, leading to materials that cannot be easily re-shaped or recycled. Physical crosslinking relies usually on the synthesis of block copolymers with hard domains insuring the network formation (polymer blocks with high softening temperature) and soft domains imparting the elastomeric behavior to the materials. In this case even if the materials can be easily re-processed, their properties may be highly affected by processing conditions that will influence the optimization of phase segregation while creeping within the hard segments is also often observed.
This communication aims at describing a new concept for the preparation of well defined reversibly crosslinked materials based on the formation of reversible carbon-carbon bonds.
Multiarm star shaped poly(ε-caprolactones) have been selectively modified at their chain end by either a diene (furan, anthracene,…) or maleimide as a dienophile, then melt processed and cured in order to form well defined thermally reversible semicristalline polymer networks exhibiting excellent shape-memory properties[1] as studied by cyclic tensile thermomechanical analysis. Reversibility of the network formation has been assessed by rheology (not shown in this abstract) and by recycling experiment.
In another approach (not developed in this abstract), poly(dimethylsiloxane-co-methyl-3-propylaminesiloxane) has been reacted with 7-chlorocarbonylmethoxy-4-methylchromen-2-one to obtain a PDMS-based polymer able to crosslink upon UV irradiation (> 310 nm) by [2+2] cyclodimerization of the 4-methylchromen-2-one (methylcoumarin) moieties. The dimers can be cleaved upon UV irradiation (< 300 nm). The reaction has been followed by rheology and by fluorescence microscopy on patterned crosslinked silicon rubbers.

2. Experimental

Materials

Toluene, dichloromethane (CH_2Cl_2) and diethyl ether from Chem-Lab as well as *N*,*N*-dimethylformamide (DMF, Aldrich), succinic anhydride, triethylamine (NEt_3), furfuryl alcohol, 9-hydroxymethyl anthracene, 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BIS-MAL), dicyclohexylcarbodimide (DCC) and 4-dimethylaminopyridine (DMAP) from Aldrich were used as received. 4-(2-hydroxyethyl)-10-oxa-4-aza-tricyclo[5.2.1.0]dec-8-ene-3,5-dione was synthesized as reported elsewhere.[2] α,ω–PCL-diol (Mn=4000; PCL-2OH) and 4-arm star-shaped PCL bearing hydroxyl groups at the end of each arm (M_n=8000 g/mol, PCL-4OH) were kindly provided by Perstorp-caprolactones.

Synthesis of end-functional functional PCL (see Figure 1)

Synthesis of 4-arm star-shaped carboxylic acid-bearing PCL (PCL-4COOH)
Typically, 80 g (40 mmol of hydroxyl function) of PCL-4OH were transferred into a previously dried glass reactor. After three azeotropic distillations with toluene, 320 ml of anhydrous DMF were added to the reactor through a rubber septum with a stainless steel capillary. After complete solubilisation, 4.4 g (44

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mmol) of succinic anhydride and 6.2 ml (44 mmol) of triethylamine were sequentially added to the DMF solution. The solution was then stirred at 45°C overnight. PCL-4COOH was recovered by precipitation in diethyl ether, filtered and dried under vacuum. Functionalization was assessed by 1H-NMR characterization .

Synthesis of 4-arm star-shaped furan-bearing PCL (PCL-4FUR)

40 g (20 mmol of carboxylic acid functions) of PCL-4COOH were transferred into a previously dried glass reactor. 150 ml of anhydrous CH_2Cl_2 were transferred to the reactor through a rubber septum using a stainless steel capillary. After the solubilisation of the PCL, 2.4 ml (22 mmol) of furfuryl alcohol, 4.5 g (22 mmol) of DCC and 0.27 g (2.2 mmol) of DMAP were transferred inside the reactor. After one night of reaction at room temperature and filtration of the formed dicyclohexylurea (DCU), PCL-4FUR was recovered by precipitation in diethyl ether, filtered and dried under vacuum. The same experimental procedure was used to prepare 4-arm star-shaped anthracene-bearing PCL (PCL-4ANTHR), using 9-hydroxymethyl anthracene instead of furfuryl alcohol as well as α,ω–bis(furan) functionalized PCLs (using the PCL-diols). Functionalization was assessed by ^{1}H-NMR characterization

Synthesis of 4-arm star-shaped maleimide-bearing PCL (PCL-4MAL)

40 g (20 mmol of carboxylic acid functions) of PCL-4COOH were transferred into a previously dried glass reactor. 150 ml of anhydrous CH_2Cl_2 were transferred to the reactor through a rubber septum using a stainless steel capillary. After the solubilisation of the PCL, 2.2 g (22 mmol) of 4-(2-hydroxyethyl)-10-oxa-4-aza-tricyclo[5.2.1.0]dec-8-ene-3,5-dione, 2.2 g (21 mmol) of DCC and 0.26 g (2.1 mmol) of DMAP were transferred inside the reactor. After one night of reaction at room temperature and filtration of the formed DCU, the protected PCL-4MAL was recovered by precipitation in diethyl etherpcl-, filtered and dried under vacuum. The polymer was then transferred into a glass reactor before to be heated at 105°C under vacuum for 10 hours to eliminate furan and regenerate the maleimide functions. PCL-4MAL was kept at room temperature. Functionalization was assessed by ^{1}H-NMR characterization.

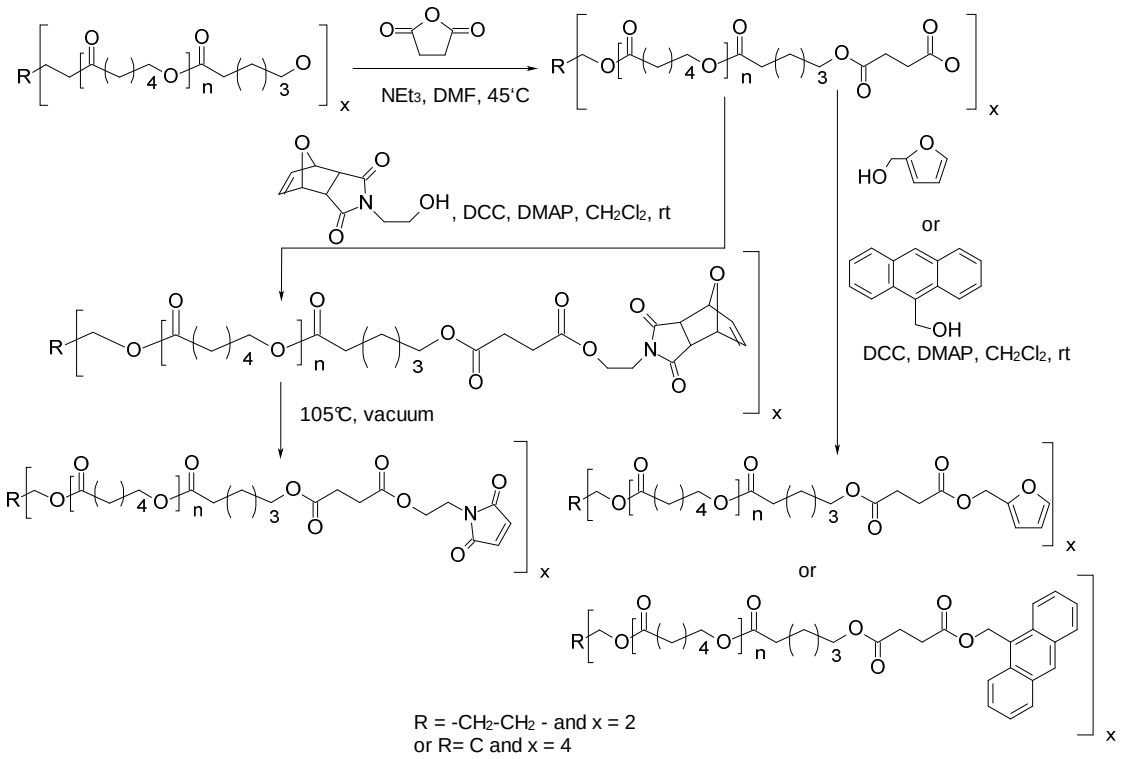

Figure 1 : Synthetic pathways for the preparation of PCL reversible network precursors

Preparation of the PCL networks

Typically, 2.2 g of PCL-4FUR and 2.2g of PCL-4MAL were melt blended at 105°C in a 6 ccm co-rotating twin screw mini-extruder (Xplore, DSM) for 15 min at 150 rpm. The extruded materials was then placed in a 0.65mm thick frame and placed under a load of 10kg in a ventilated oven at 65°C for 72h. The sample is recovered in form of a flat sheet that is kept min 48h at room temperature before measurement.
The same procedure (but respecting the stoichiometric amount between the materials) was followed when using difunctional PCL (PCL-2FUR) or PCL-4ANTHR instead of PCL-4FUR and BIS-MAL instead of PCL-4MAL.

Characterization techniques

Size exclusion chromatography (SEC) was carried out in THF at 45°C at a flow rate of 1 mL/min with a SFD S5200 auto sampler liquid chromatograph equipped with a SFD refractometer index detector 2000. The PL gel 5µm (10^5 Å, 10^4 Å, 10^3 Å and 100 Å) columns were calibrated with polystyrene standards. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz in the FT mode with a Bruker AN 400 apparatus at 25°C. Shape memory properties have been measured with a DMA Q800 (TA Instruments) using the tensile film clamp in controlled force mode. The sample (typically 4mm x 5mm x 0.65 mm) was first equilibrated at 65°C for 5 min then experienced a tensile stress ramp (0.06 MPa/min) till 0.6 MPa. Then, the sample is cooled down, under stress at 3°C/min to 0°C and maintained at that temperature for 5 min. The stress is then released and the sample is reheated, stress-free at 3°C/min to 65°C. The process is cycled 4 times.

3. Results & Discussion

A linear PCL terminated by a hydroxyl group at each chain end with a molecular weight of 4000 g/mol (PCL-2OH) and a 4-arm star-shaped PCL with a molecular weight of 8000 g/mol (PCL-4OH) also functionalized by a hydroxyl group at each chain end were selected as precursors to generate the thermo-reversible networks. The chain-ends of these different PCLs were selectively converted into diene (furan or anthracene) or dienophile (maleimide) by a two steps process following the synthetic pathway depicted in Fig. 1. The molecular characteristics of the polymers are given in Table 1.

Table 1. Molecular characteristics of the starting and functionalized PCLs

PCLs	**End-function**	**Mn, SEC [a] [g/mol]**	**Mw/Mn, SEC**	**% function [b] [%]**
PCL-2OH	Hydroxyl	7800[c]	1.35	100
PCL-4OH	Hydroxyl	14000	1.18	100
PCL-2FUR	Furan	8800[c]	1.25	85
PCL-4FUR	Furan	16800	1.30	87
PCL-4MAL	Maleimide	16400	1.22	85
PCL-4ANTHR	Anthracene	N.D.	N.D.	83

[a] PS standards; [b] as calculated from ^{1}H-NMR spectra; [c] PCL mass, following Mark Houwink equation : M_n (PCL) = 0.29 $M_n(PS)^{1,703}$; N.D. : not determined

PCL-furan and PCL-maleimide was melt blended into a mini-extruder at 105°C. This temperature was chosen in order to favor the retro-Diels-Alder reaction during blending and so avoiding any cross-linking into the mixing chamber.[3] After extrusion, the mixing was rapidly injected into a mold in order to confer an identical and well-defined shape to each sample. These samples were then cut into five pieces having the same weight before to be introduced into a thermostated oven at 65°C in order to favor the Diels-Alder reaction[3] leading to the cross-linking of the material. The kinetic of reaction was followed by measurement of the swelling rate (and the amount of insolubles) of the material in $CHCl_3$, in function of reaction time (up to 7 days), for three systems : PCL-2FUR/PCL-4MAL, PCL-4FUR/BIS-MAL; PCL-4FUR/PCL-

4MAL. For the PCL-2FUR/PCL-4MAL, the swelling test leaded to the dissolution of the samples, whatever the curing time. SEC analysis of the obtained material revealed a very large and multimodal molar mass distribution, at larger masses than the precursors, indicating the probable formation of a hyperbranched structure. The two other systems leaded to the formation of a gel when swollen in $CHCl_3$, allowing for the study of the crosslinking reaction. The swelling rate and the fraction of insoluble materials with reaction time are reported in Figure 2.

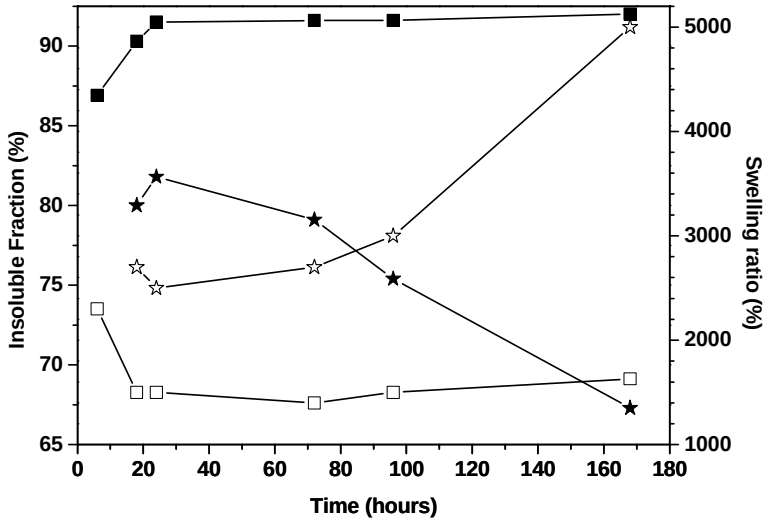

Figure 2. Evolution of the swelling ratio (open) and the insoluble fraction (plain) for the PCL-4FUR/BIS-MAL(star) and the PCL-4FUR/PCL-4MAL (square) systems with curing time.

On the basis of these results, several observations can be made. First, the rate of crosslinking was larger for the PCL-4FUR/PCL-4MAL system than for the PCL-4FUR/BISMAL as indicated by the larger swelling ratio and the lower insoluble fraction recorded for the latter. Moreover, the PCL-4FUR/BISMAL system showed a constant decrease in the crosslinking degree after 24h of curing. These observations can be rationalized by the combination of three factors : the dynamic equilibrium between Diels Alder and retro-Diels Alder reactions at 65°C for the furan/maleimide couple; the low functionality and molar mass of the BIS-MAL molecule (only 2 maleimide moieties) and the poor solubility of BIS-MAL in PCL. The dynamic equilibrium coupled to the low functionality statistically favor the liberation of the molecule and its low mass and weak affinity for PCL allows for its phase segregation during curing, impeding its reaction with furan moieties borne on PCL. The PCL-4FUR/PCL-4MAL was characterized by a much higher degree of crosslinking (lower swelling ratio, larger insoluble fraction) with the optimum values obtained after 72 hours. Therefore, this last couple, crosslinked under these optimized conditions, has been used for the preparation of chemically-crosslinked yet recyclable shape memory candidate material.

Figure 3 shows the qualitative and the quantitative characteristics of the shape memory properties of the crosslinked PCL-4FUR/PCL-4MAL sample. Above the melting point of PCL, the sample could be manually elongated to about 5x its initial length and kept its temporary shape upon cooling. Then, when immerged in water at 60°C, it instantaneously recovered its initial (permanent) shape (Fig. 3a). Cyclic tensile testing (Fig. 3b) allowed to better appreciate the behavior of the material. In the loading phase at 65°C, the sample deformed relatively linearly. Upon cooling under constant stress, the sample first crept until reaching ca. 20°C then, between 20°C and 0°C, the sample experienced a large increase of its deformation, due to the oriented crystallization of the PCL chains. Upon unloading, the sample displayed very high fixing properties (fixity above 99% for each cycle). Then upon heating, the sample recovered its permanent shape when the sample was exposed at temperatures above ca. 54°C (switching temperature). The first cycle is characterized by an incomplete recovery (88%), known as training phenomenon, while the following cycles are characterized by a recovery above 99%. However, it can be observed on Fig.3b that, when increasing the number of cycles, the ability of the sample to deform increases. This particular phenomenon is explained by the occurrence of retro Diels Alder reactions at 65°C. Therefore during

loading at 65°C, some Diels Alder bonds broke and the stretched chains relaxed, pulling away the Diels Alder reactants that are not able then to rebuild the bond during the cycle. At each cycle, the phenomenon occurs, the materials is slightly less crosslinked and therefore more ductile.

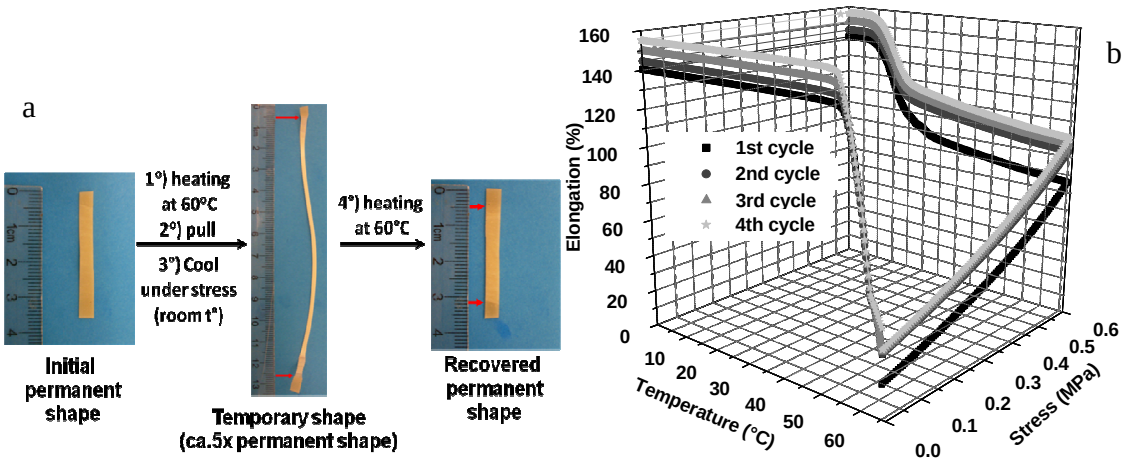

Figure 3. Shape memory behavior in tensile testing for PCL-4FUR/PCL-4MAL : a. qualitative (manual stress); b. quantitative (DMA analysis)

In order to avoid this phenomenon, the use of a Diels-Alder couple characterized by a higher temperature for retro Diels Alder initiation is required. This is the case for the anthracene /maleimide couple which retro Diels Alder initiation temperature is well above 180°C.[4] Thus, PCL-4ANTHR/PCL4-MAL sample has been prepared using the same conditions (melt blending stoichiometric amounts in a mini-extruder then prepare a film at 65°C for 72 hours). Figure 4 shows the resulting shape memory cyclic tensile testing.

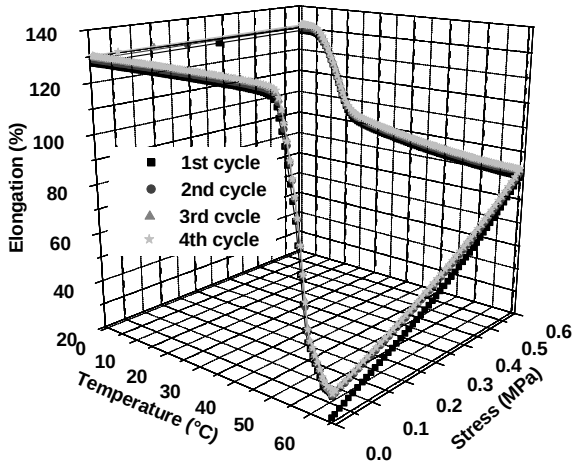

Figure 4. Shape memory behavior in tensile testing for PCL-4ANTHR/PCL-4MAL sample

The PCL-4ANTHR/PCL-4MAL sample showed also highly performant shape memory properties with optimal fixity (>99%) and recovery (>99%) for cycle 2, 3 and 4 (cycle 1 has a recovery of 92%) and the switching temperature at 52°C. Interestingly, due to the much higher temperature for retro Diels Alder initiation, the sample does not softens with the cycles but this high temperature does not allow recycling, due to the relatively weak thermal stability of the functional PCLs at the temperature requested for being in the retro Diels Alder regime.

This is not the case for the PCL-4FUR/PCL-4MAL sample that has been successfully reshaped by melting the chopped shape memory film in the cylinder of a DSM mini-injection device for 20 min at 125°C, re-injected in form of a barrel, hot pressed and crosslinked again at 65°C for 72 hours in a film and measured in tensile mode for shape memory properties (Figure 5).

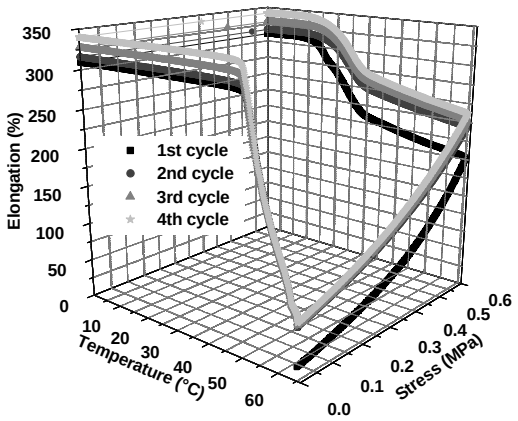

Figure 5. Shape memory behavior in tensile testing for recycled PCL-4FUR/PCL-4MAL sample

The recycled PCL-4FUR/PCL-4MAL still exhibits shape memory properties with excellent fixity (>99%) and recovery (>99%) for cycle 2, 3 and 4 and correct recovery () for the first cycle. However, the sample is characterized, as compared with the initial sample, by a much higher deformation (around 325% compared to 145%), indicating a probably reduced degree of crosslinking. This is thought to be due to possible degradation of one or the other of the Diels Alder reactants upon recycling conditions (exposure to 125° for 20 min in air). Such phenomenon might be reduced by either proceed to the retro-Diels Alder reaction under inert conditions or by adding adequate stabilizers in the formulation.

4. Conclusions

Diels Alder reaction can be used to prepare PCL-based thermoreversible networks exhibiting excellent shape memory properties. Most efficient crosslinking was obtained when mixing equimolar quantities of 4-arm star shaped PCLs functionalized with complementary maleimide and furan or anthracene moieties. Shape memory properties have been assessed by cyclic tensile thermomecanical measurement and virtually complete fixity and total recovery were recorded in the three cycles following the first one (training effect). Softening of the material is observed for the furan/maleimide Diels Alder couple, due to a too low cycloreversion initiation temperature while this phenomenon is absent for the anthracene/maleimide couple, known to yield to much more thermally stable Diels Alder adducts. This high stability impedes the recycling of the crosslinked materials while partial recyclability is demonstrated for the furan/maleimide sample. The research for Diels Alder couples with more adapted cycloreversion initiation temperature are under current investigation, as well as the effect of the PCL branches molar masses on the mechanical and shape memory properties of this new type of material.

5. References

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